OBSERVATIONS OF DISLOCATIONS IN ZINC BY CHEMICAL ETCHING

J. Wayne Miller, Norio Nagata* and T. Vreeland, Jr.

W. M. Keck Laboratories, California Institute of Technology
Pasadena, California 91109

ABSTRACT

A new chemical etch has been found to be effective for revealing dislocations intersecting the basal planes of zinc. The technique works for crystals whose orientation is within 0.70° of the basal plane. Evidence is available that there is a one to one correspondence between etch figures and dislocations. Crystals with densities as high as 10^7 dislocations per cm^2 have been successfully etched.

*On leave from the National Research Institute for Metals, Tokyo, Japan

Introduction

Chemical etching to reveal dislocations in crystals is a valuable tool for studying these dislocations. Many successful etches for various materials are available[1] but the understanding of the complex chemical mechanism on the metal surface is, at best, only qualitative. Numerous articles have been published on etching zinc crystals[2-6] but the etches for (0001) surfaces were found not to be very reliable in this study. The etches of references 4-6 require high concentrations of solute impurities and will not be further discussed since an etch that reveals undecorated dislocations is of interest.

Rosenbaum[2] has made the most comprehensive study for the etching of the (0001) basal plane. We found his recommended etching solution of 25ml ethanol and 1.5ml of 48% hydrobromic acid works well for freshly cleaved surfaces but it did not work reliably on crystals which were acid lapped or chemically or electrolytically polished. We also found the short etching time of about one second made the etching processs hard to control. It is often desirable to polish and re-etch specimens several times and an etching technique which works well on polished as well as on cleaved surfaces is then needed.

In this report a chemical etch technique will be given for etching surfaces of zinc crystals near the (0001) basal plane. The etch does not depend on impurities and is less sensitive to orientation that those previously reported for the (000) plane.

Experimental Procedures

Monocrystals grown by the Bridgeman method in pyrex molds coated with graphite were used in this work. The material was 99.999% zinc obtained from the New Jersey Zinc Company.

Specimens were made into right circular cylinders and retangular prisms by methods previously described(7). A final electro-polishing step was used just prior to etching to flatten the surface and remove surface films. The crystal was electro-polished in a solution containing three parts ethanol and one part concentrated nitric acid by volume at 1.5 volts for twenty seconds with mild agitation. Various etching procedures were then carried out and the specimen surfaces were examined optically at magnifications between 40 and 500X. Water, ethanol and methanol were used as solvents in the etching solutions. The reactive etchants used were hydrofloric acid, hydrobromic acid, hydrochloric acid, acetic acid, formic acid, bromine and iodine.

Results

Attempts to use previously described solutions did not give reliable etching patterns and there was often a question as to whether the etch patterns were dislocations. A solution of 30ml ethanol, 1 ml of 48% hydrobromic acid and 1 ml of bromine was found to be the most reliable etchant. The solution has a useful shelf life of several days if the container is kept closed.

The etching time is a function of the temperature of the crystal and solution. The etching times for a specimen at various temperatures and a room temperature solution are: 1 second at room temperature, 5 seconds at 0°C and 10-12 seconds at -70°C. Best results were obtain at the lower temperature because the longer time gave a more controllable etch.

The procedure for cooling the specimen down to the dry ice temperature is to mildly agitate the crystal in an ethanol bath at -70°C for five minutes. The crystal is quickly dried with a stream of air before etching. The crystal is etched 10-12 seconds depending on the dislocation density (shorter times for high densities) and brought up to room temperature under running water. A distilled water rinse follows and finally the crystal is dried in a stream of air. The resulting etch leaves a film-free surface.

Attempts to use a cooled solution and crystal, both at -70°C, did not offer much improvement as the solution became viscous and the crystal did not etch in thirty seconds. If the solution is cooled to -70°C and the crystal is at room temperature, the etching time is 3 seconds. Increased dilution of the solution gave slightly increased etching times but the pits became shallower and the results were not satisfactory.

The cooling and heating procedures were checked to see if any basal dislocations were produced by thermal stresses. These basal dislocations are visible within 2.5μ of the basal plane surface with the Berg-Barrett X-ray diffraction method[8]. A newly cleaved and annealed crystal was cooled for five minutes in ethanol at -70°C and warmed to room temperature under running water as described. A Berg-Barrett X-ray diffraction photograph was taken of the crystal and the results indicated that no basal dislocations appeared.

The etch pits on the basal plane are hexagonal in shape and have a star-like appearance when viewed under an optical microscope. A few hexagonal pits with flat bottoms as seen in Figure 1 occur because of general surface etching. These pits are not included in dislocation density counts. These pits are not included in dislocation density counts. Oblique lighting is useful in determining which pits have flat bottoms. The radial arms of the dislocation etch figure are parallel to the $\langle 11\bar{2}0 \rangle$ directions.

As the surface orientation deviates from the basal plane, the star-like shape becomes less symmetrical. Figure 2 shows a segment of an etched spherical surface. The deviation in degrees from the basal plane is shown in the figure. These measurements were made with a modified Unitron microgoniometer. The angle where one-half of each etch pit has disappeared is $0.70° \pm 0.05°$. This angle is close to the angle which the wall of the etch pit makes with the basal plane and beyond this limit, dislocations are not revealed.

Crystals were deformed by various means to check the correspondence of etch pits to dislocations. Crystals were twinned as described by Blish and Vreeland[9] and etched after twinning (Figure 3). The dislocation densities measured in the vicinity of the twin was 10^7 cm^{-2}. Crystals were compressed uniaxially and perpendicular to the $\langle \bar{1}2\bar{1}0 \rangle$ basal slip directions. The correspondence of etch pits to dislocations was as expected and is discussed later.

Discussion

The evidence which suggests that there is a one to one correspondence of etch pits and dislocation pits is:

1) Fresh dislocations produced by twinning a crystal on the basal plane at room temperature have the expected dislocation distribution around the twins: accomodation kinks, dislocations aligned with and ahead of twin traces, and the appearance of dislocations

in bands on second-order pyramidal planes. Dislocation densities are also similar to those observed by Blish and Vreeland[9].

2) Fresh dislocations introduced by compression perpendicular to the $\langle \bar{1}2\bar{1}0 \rangle$ basal slip bands on the (0001) surface. The dislocation densities increased with increasing strain.

3) Sub-grain boundaries and grown-in dislocation etch.

The exact chemistry of the surface reaction is unknown but might be postulated similar to that proposed by Rosenbaum[2]. The hydrogen ion (H^+) oxidizes the zinc surface by the reaction

$$2\,H^+ + Zn = H_2 + Zn^{+2}$$

and the bromine acts as a moderator for the reaction. The exact role of the bromine is unclear but it is probably similar to a weak poison from a catalytic-chemistry viewpoint.

Summary

The etch meets the criteria for which it was developed:

1. Controllable etching times.
2. Ability to reliably etch surfaces oriented with 0.70° of the (0001) basal plane of zinc.
3. A one to one correspondence of etch pits and dislocations.

References

1. W. H. Robinson, "Techniques of Metals Research" Vol. II pp. 291-340 R. F. Bunshak, Interscience, New York (1968).
2. H. S. Rosenbaum and M. M. Saffren, J. Appl. Phys., 32, 1866 (1961).
3. R. C. Brandt, K. H. Adams and T. Vreeland, Jr., J. Appl. Phys. 32, 591 (1961).
4. V. M. Kosevich and V. P. Soldatov, Kristallografiya, 6, 439 (1961).
5. J. J. Gilman, Trans. A.I.M.E., 206, 998 (1956).
6. G. Bassi and J. P. Hugo, J. Inst. Metals, 87, 376 (1958).
7. D. P. Pope and T. Vreeland, Jr., Trans. A.I.M.E., 245, 2447 (1969).
8. A. P. L. Turner, T. Vreeland, Jr. and D. P. Pope, Acta Cryst., 424, 452 (1968).
9. R. C. Blish and T. Vreeland, Jr., J. Appl. Phys., 39, 2290 (1968).

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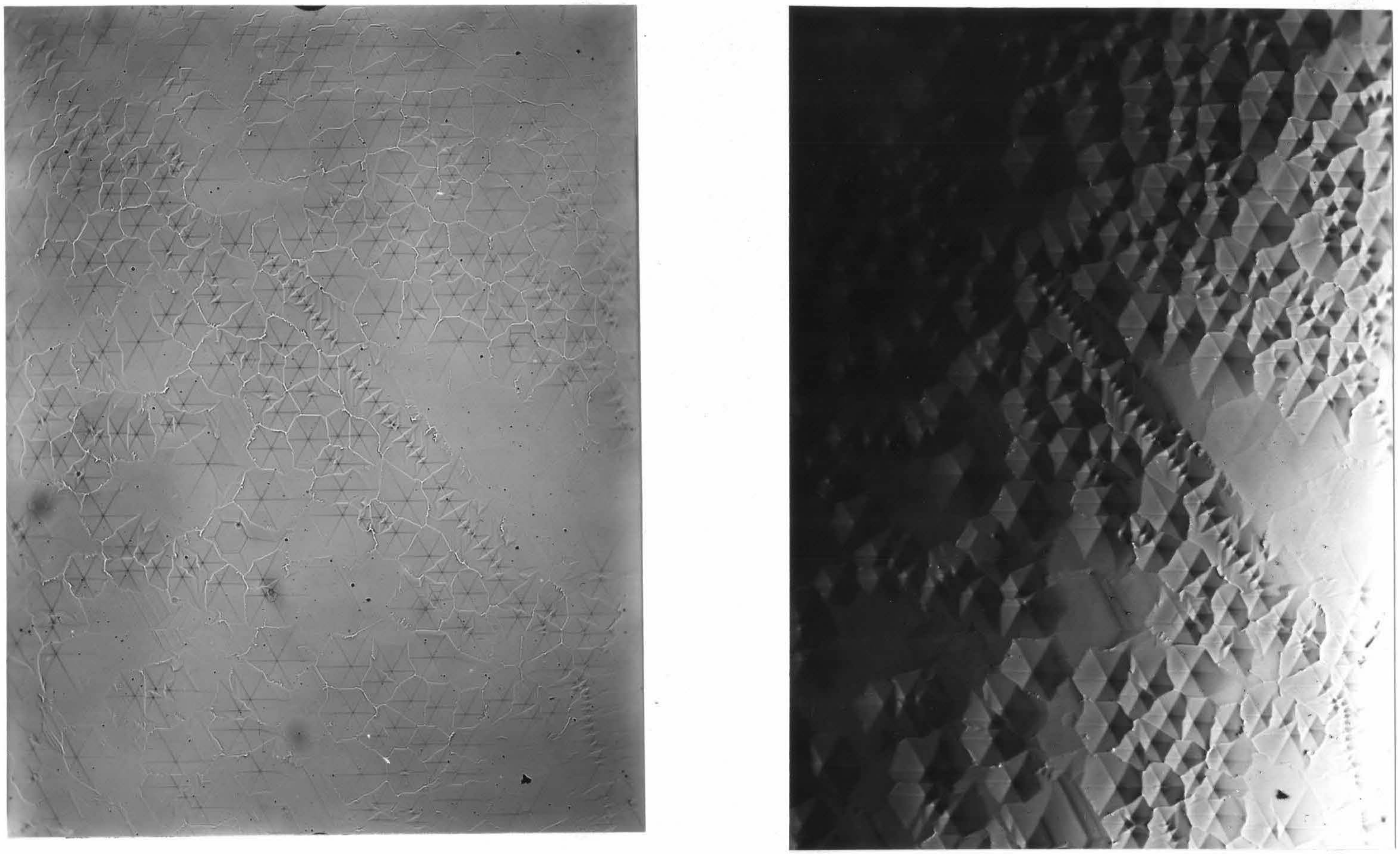
FIGURE CAPTIONS

Figure 1. (a) Area of moderate dislocation density showing a flat bottom pit. (b) Oblique lighting of same area. 100X

Figure 2. Etched surface of zinc showing dislocation etch pits and the dependence of the surface orientation. The scale indicates the angle between the surface and the (0001) basal plane (in degrees).

Figure 3. Etched surface showing dislocations around a twin.

(a) (b)



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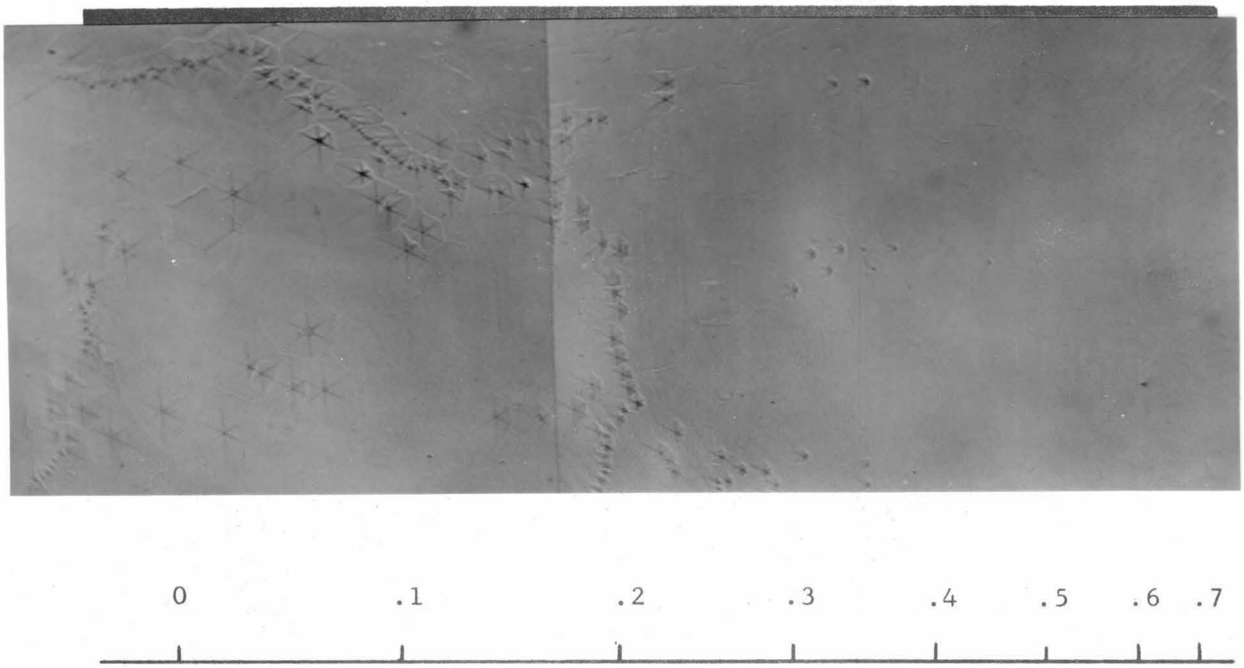

Fig. 1. Etched surface of zinc showing dislocation etch pits and the dependence of the etch surface orientation. 78X. The scale indicates the angle between the surface and the (0001) basal plane (in degrees).

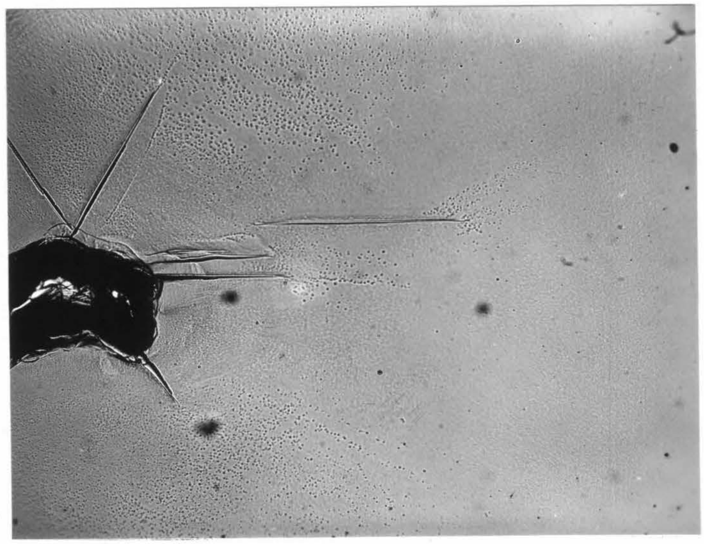

Figure 3. Etched surface showing dislocations around a twin.